# Topic 12: Entropy and Energetics

## 12A: Entropy

### Students will be assessed on their ability to:

**12.1** understand that, since endothermic reactions can occur spontaneously at room temperature, enthalpy changes alone do not control whether reactions occur

A spontaneous process takes place without continuous external intervention

It is often thought that for a reaction to occur spontaneously, the products should be more energetically stable than the reactants, which means the products should have less energy than the reactants

So, we can conclude that exothermic reactions can occur spontaneously as they release energy but what about endothermic reactions? What is the driving force behind it?

Well, the answer to that is 'entropy'

**12.2** understand entropy as a measure of disorder of a system in terms of the random dispersal of molecules and of energy quanta between molecules

**Entropy(S)** is a *measure of disorder of a system in terms of the random dispersal of molecules and of energy quanta between molecules*

- An increase in entropy means that the system is more energetically stable as the energy of the system is more spread out when it's in a disordered state

**12.3** understand that the entropy of a substance increases with temperature, that entropy increases as solid → liquid → gas and that perfect crystals at zero kelvin have zero entropy

1. The 1st Law of Thermodynamics (Law of Energy Conservation):
   *Energy can neither be created nor destroyed, only transferred from one form to another*
2. The 2nd Law of Thermodynamics (Entropy Law):
   *In a spontaneous process, the total entropy tends to increase*
3. The 3rd Law of Thermodynamics (Absolute Zero Law):
   *The entropy of a perfect crystal at the temperature of absolute zero (0K) is zero*

Entropy also depends on $A_r$ (the higher the atomic mass, the greater the entropy)
For eg:
$S(He) < S(O_2)$

Usually, entropy increases with increasing volume or decreasing concentration/ pressure

Distribution of Energy

- Energy exists in packets called 'quanta' which are whole numbers
- The distribution of quanta between molecules is random so the more quanta there are, the more ways of arranging them between molecules
- The more molecules there are, the more ways there are of sharing the quanta

Entropy of a substance increases with temperature

- The higher the temperature, the more energy a substance has
- The more energy a substance has, the more ways there are to distribute energy between molecules
- The more ways of distribution of energy, the higher the entropy

Entropy of a substance increases as solid → liquid → gas

- In the solid state, particles are fixed in place and can only vibrate but in the liquid state, they are still closely packed together but are arranged randomly which means it is more disordered
- Gases are the most disordered, then come liquids and then solids

Perfect crystals at 0K (absolute zero) have 0 entropy

- A perfect crystal has an internal lattice structure that is always the same
- The particles are fixed and are not moving

**12.4** be able to interpret the natural direction of change as being in the direction of increasing total entropy (positive entropy change), including gases spread spontaneously through a room

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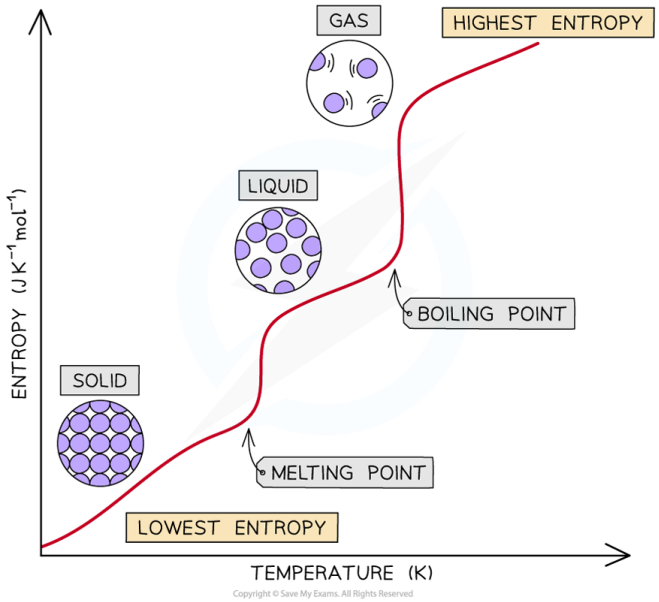
| | **Entropy** is a description of the number of ways atoms can share quanta of energy<br>If the number of ways of arranging the atoms and energy (W) is high, then system is disordered, and entropy (S) is high<br>The relationship between W and S is: $S = k\ln W$<br>The natural direction of change is in the direction of increasing total entropy |
| **12.5** | understand why entropy changes occur during:<br>i changes of state<br>ii dissolving of a solid ionic lattice<br>iii reactions in which there is a change in the number of moles from reactants to products |
| **i** | Entropy of a substance changes with changes of state<br>In general, entropy increases in the order: solid < liquid < gas (and vice versa)<br>  <br>When a substance increases in temperature, its entropy increases as the particles have more energy, so they vibrate/arrange themselves more randomly resulting in increased disorder<br>There is a bigger jump in entropy with boiling than that with melting<br>Gases have large entropies as they are much more disordered<br><br>For endothermic reactions, $\Delta S_{surroundings}$ is negative<br>For exothermic reactions, $\Delta S_{surroundings}$ is positive<br>When solid → liquid/gas or liquid → gas, $\Delta S_{system}$ is positive<br>When gas → liquid/solid or liquid → solid, $\Delta S_{system}$ is negative |
| **ii** | When an ionic solid dissolves in water:<br>- The lattice structure is broken down<br>- The ions become hydrated<br>The breaking down of lattice structure is an endothermic process (reverse of lattice energy) and results in an increased number of moles of particles which means an increase in the level of disorderness and hence, an increase in entropy of the salt ($\Delta S_{system}$ is positive)<br>The hydration of the ions is an exothermic process but results in the water molecules becoming more ordered as they arrange themselves in an orderly manner around the positive and negative ions which results in a decrease in the entropy of water ($\Delta S_{surroundings}$ is negative)<br>The solubility of an ionic solid is determined by the total entropy change for the solid which in turn means: $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = \Delta S_{system} - \Delta_{sol}H / T$ |

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| Elements | *...tend to have lower entropies than...* | Compounds |
| Simpler compounds | | Complex compounds |
| Pure substances | | Mixtures |

**iii** When the number of moles is increased, the number of particles present is increased which results in an increase in the number of ways that the particles can be arranged which then increases the entropy of the system, making $\Delta S_{system}$ positive

**EXAMPLE 1**

$$2CH_3COOH(l) + (NH_4)_2CO_3(s) \rightarrow 2CH_3COONH_4(s) + H_2O(l) + CO_2(g)$$

Number of moles of reactants = 3

Number of moles of products = 4

So, $\Delta S_{system}$ is positive.

**EXAMPLE 3**

$$Mg(s) + \tfrac{1}{2}O_2 \rightarrow MgO(s)$$

Number of moles of reactants = 1.5

Number of moles of products = 1

So, $\Delta S_{system}$ is negative.

**12.6** understand that the total entropy change of any reaction is the sum of the entropy change of the system and the entropy change of the surroundings, summarised by the expression:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

Unit is in J $K^{-1}$ $mol^{-1}$

$\Delta S_{system} = \Sigma S(products) - \Sigma S(reactants)$

When solid → liquid/gas or liquid → gas, $\Delta S_{system}$ is positive

When gas → liquid/solid or liquid → solid, $\Delta S_{system}$ is negative

$$\Delta S_{surroundings} = \frac{-\Delta_{sol}H}{T}$$

For endothermic reactions, $\Delta S_{surroundings}$ is negative

For exothermic reactions, $\Delta S_{surroundings}$ is positive

**12.7** be able to calculate the entropy change of the system for a reaction, $\Delta S_{system}$, given the entropies of the reactants and products

Predicting $\Delta S_{system}$ Qualitatively

An **increase** in disorder and **entropy** will lead to a positive entropy change $\Delta S^{\circ}_{system}$ **= +ve**

Balanced chemical equations can often be used to predict if $\Delta S^{\circ}_{system}$ is positive or negative.

**In general,** a significant increase in the entropy will occur if:
-there is a ***change of state*** from **solid or liquid to gas**
- there is a significant ***increase in number of molecules*** between products and reactants.

$NH_4Cl(s) \rightarrow HCl(g) + NH_3(g)$
$\Delta S^{\circ}_{system}$ **= +ve**
•change from solid reactant to gaseous products
•increase in number of molecules
both will increase disorder

$Na_{s} + \frac{1}{2} Cl_{2\,g} \rightarrow NaCl_{s}$
$\Delta S^{\circ}_{system}$ **= -ve**
•change from gaseous and solid reactant to solid
•decrease in number of molecules
both will decrease disorder

Calculating $\Delta S_{system}$ Quantitatively

Data books lists standard entropies ($S^{\circ}$) **per mole** for a variety of substances. It is not possible for a substance to have a standard entropy of less than zero.

Elements in their standard states do *not* have zero entropy. **Only perfect crystals at absolute zero ($T$ = 0 K) will have zero entropy:**

The unit of entropy is **J $K^{-1}$ $mol^{-1}$**

$$\Delta S^{\circ}_{system} = \Sigma S^{\circ}_{products} - \Sigma S^{\circ}_{reactants}$$

**Example**

Calculate $\Delta S^{\circ}$ for the following reaction at 25°C:

$2Fe_2O_3(s) + 3C(s) \rightarrow 4Fe(s) + 3CO_2(g)$

$\Delta S^{\circ}_{system} = \Sigma S^{\circ}_{products} - \Sigma S^{\circ}_{reactants}$

$= (3 \times 213.6 + 4 \times 27.3) - (2 \times 87.4 + 3 \times 5.7)$

$= +558.1$ J $K^{-1}$ $mol^{-1}$ = **+ 558 J $K^{-1}$ $mol^{-1}$** (3 S.F.)

S $[Fe_2O_3]$ = 87.4 J $K^{-1}$ $mol^{-1}$
S [C] = 5.7 J $K^{-1}$ $mol^{-1}$
S [Fe] = 27.3 J $K^{-1}$ $mol^{-1}$
S $[CO_2]$ = 213.6 J $K^{-1}$ $mol^{-1}$

Note: the entropy change is very positive as a large amount of gas is being created increasing disorder

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| **12.8** | be able to calculate the entropy change in the surroundings, and hence $\Delta S_{total}$, using the expression $\Delta S_{surroundings} = \frac{-\Delta H}{T}$ |
| | For an exothermic reaction, $\Delta H$ is negative, $\Delta S_{surroundings}$ will always be positive as energy is released to the surroundings which means the number of ways of arranging the energy quanta between particles increases<br>For an endothermic reaction, $\Delta H$ is positive, $\Delta S_{surroundings}$ will always be negative as the energy is absorbed from the surroundings which means the number of ways of arranging the energy quanta between particles decreases |
| **12.9** | understand that the feasibility of a reaction depends on:<br>i the balance between $\Delta S_{system}$ and $\Delta S_{surroundings}$, so that even endothermic reactions can occur spontaneously at room temperature<br>ii temperature, as higher temperatures decrease the magnitude of $\Delta S_{surroundings}$ so its contribution to $\Delta S_{total}$ is less<br>*Students should be able to calculate the temperature at which a reaction is feasible.*<br>*Students may also use $\Delta G = \Delta H - T\Delta S_{system}$ in answers, although this approach is not a requirement of the specification.* |
| **i** | For $\Delta S_{total}$ to be positive and therefore the reaction feasible:<br>▪ Both $\Delta S_{system}$ and $\Delta S_{surroundings}$ are positive<br>▪ $\Delta S_{surroundings}$ is positive and $\Delta S_{system}$ is negative, but $\Delta S_{surroundings} > \Delta S_{system}$<br>▪ $\Delta S_{surroundings}$ is negative and $\Delta S_{system}$ is positive, but $\Delta S_{surroundings} < \Delta S_{system}$<br>Feasibility at a certain temperature (tendency of a reaction to occur spontaneously without external influence) depends on enthalpy($\Delta H$) and entropy change ($\Delta S_{total}$)<br>(Generally, $\Delta S_{total}$ should be *positive* and/or $\Delta H$ should be *exothermic*) |
| **ii** | Higher temperatures decrease the magnitude of $\Delta S_{surroundings}$ so its contribution to $\Delta S_{total}$ is less<br>Gibbs free energy!<br>No longer a requirement of the specification but it's useful to know just in case!<br>Gibbs free equation combines $\Delta H$ and $\Delta S_{system}$ into one equation to show their relationship: $\Delta G = \Delta H - T\Delta S_{system}$<br>Units are in kJ $mol^{-1}$<br>For a reaction to be feasible, $\Delta G \leq 0$ |
| **12.10** | understand that reactions can occur as long as $\Delta S_{total}$ is positive even if one of the other entropy changes is negative |
| | $\Delta S_{total}$ will be positive if:<br>• both $\Delta S_{surroundings}$ and $\Delta S_{system}$ are positive<br>• $\Delta S_{surroundings}$ is positive and $\Delta S_{system}$ is negative, but the magnitude of $\Delta S_{surroundings}$ > the magnitude of $\Delta S_{system}$<br>• $\Delta S_{surroundings}$ is negative and $\Delta S_{system}$ is positive, but the magnitude of $\Delta S_{surroundings}$ < the magnitude of $\Delta S_{system}$. |

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| **12.11** | understand and distinguish between the concepts of thermodynamic stability and kinetic stability |
| | Thermodynamically stable<br>- Depends upon whether or not a reaction is spontaneous<br>- Reaction is feasible if the total entropy is positive<br>Kinetically stable<br>- Depends on the rate of reaction and activation energy ($E_a$)<br>- Reactions which have a high $E_a$ will not take place at room temperature<br>A reaction mixture is said to be kinetically stable if it will not take place spontaneously at room temperature due to high activation energy even if it is thermodynamically favorable |
| | **Further suggested practicals**<br>Investigate chemical reactions in terms of disorder and enthalpy change, including:<br>I dissolving a solid, including adding ammonium nitrate crystals to water<br>Ii gas evolution, including reacting ethanoic acid with ammonium carbonate<br>Iii exothermic reaction producing a solid, including burning magnesium ribbon in air<br>iv endothermic reaction of two solids, including mixing solid barium hydroxide, $Ba(OH)_2.8H_2O$ with solid ammonium chloride |

## 12B: Lattice energy

**Students will be assessed on their ability to:**

**12.12** be able to define the terms:

I standard enthalpy change of atomisation, $\Delta_{at}H$

ii electron affinity, EA

iii lattice energy (as the exothermic process for the formation of one mole of an ionic solid from its gaseous ions)

**$\Delta_{at}H$**: *the enthalpy change measured at a stated temperature, usually 298K, and 100kPa when one mole of gaseous atoms is formed from an element in its standard state (always endothermic)*

Common examples:

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ $\frac{1}{2}Br_2(l) \rightarrow Br(g)$

$Na(s) \rightarrow Na(g)$

Electron affinity can be thought of as the opposite of ionization energy

**EA**: *the energy change when each atom in one mole of atoms in the gaseous state gains an electron to form a -1 ion*

Common examples of first electron affinity: (mostly exothermic)

$Cl(g) + e^- \rightarrow Cl^-(g)$

$Li(g) + e^- \rightarrow Li^-(g)$

Exceptions: EA of nobles gases are endothermic

Common examples of second electron affinity: (mostly endothermic)

$O^-(g) + e^- \rightarrow O^{2-}(g)$

The more exothermic the value of Lattice Energy is, the stronger the ionic bonds within the lattice

**Lattice energy**: *the energy change measured at a stated temperature, usually 298K, and 100kPa when one mole of an ionic compound is formed from its ions in the gaseous state (always exothermic)*

Common examples:

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

$Mg^{2+}(g) + Cl^-(g) \rightarrow MgCl_2(s)$

Factors that affect Lattice energy (of formation)

1. Magnitude of charges on the ions
2. Sum of the ionic radii (distance between centre of cation to anion)
3. Extent of covalent interactions between the ions

Recall these from your AS studies:

**$\Delta_fH$**: *the enthalpy change measured at 100kPa and a specified temperature, usually 298K, when one mole of a substance is formed from its elements in their standard states*

Common examples:

$C(s) + 2H_2(g) \rightarrow CH_4(g)$

$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$

**$\Delta_cH$**: *the enthalpy change measured at 100kPa and a stated temperature, usually 298K, when one mole of a substance is completely burned in oxygen (always exothermic)*

**$\Delta_{neut}H$**: *the enthalpy change measured at 100kPa and a stated temperature, usually 298K, when one mole of water is produced by the neutralization of an acid with an alkali (always exothermic)*

**IE:** *the amount of energy required to remove one mole of electrons from one mole of gaseous atoms of an element to form one mole of gaseous ions (always endothermic)*

Example of first IE: $A(g) \rightarrow A^+(g) + e^-$

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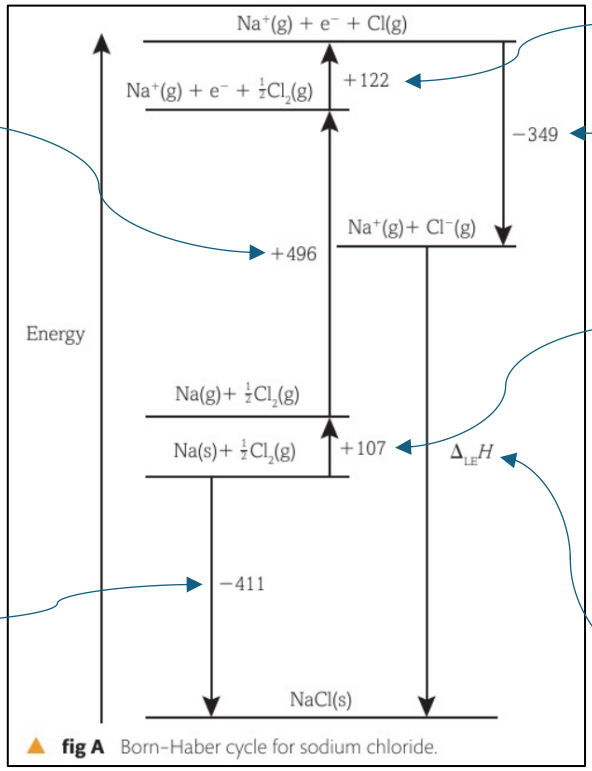
| **12.13** | be able to construct Born-Haber cycles and carry out related calculations |
| | The lattice energy cannot be determined directly<br>So, we need to calculate it indirectly by using the Born-Haber cycle<br>  <br><br>▲ **fig A** Born–Haber cycle for sodium chloride.<br>$\Delta_{at}H$ of $Cl_2$<br>1st IE of Na(g)<br>1st EA of Cl(g)<br>Arrows pointing upwards indicate an endothermic reaction while arrows pointing downwards indicate an exothermic reaction<br>$\Delta_{at}H$ of Na(s)<br>$\Delta_{f}H$ of NaCl(s)<br>Lattice Energy, $\Delta_{LE}H$ of NaCl(s)<br>It is the overall energy change involved that determines how atoms and molecules will interact with one another to form a compound (not to achieve a noble gas configuration like we were taught back in International-GCSE)<br>The overall energy change involved is influenced by changes in temperature or pressure |
| **12.14** | understand that a comparison of the experimental lattice energy value (from a Born-Haber cycle) with the theoretical value (obtained from electrostatic theory) in a particular compound indicates the degree of covalent bonding |
| | **Theoretical lattice energy** is the lattice energy calculated using the principles of electrostatics but with the following assumptions made:<br>• The ions are perfectly in contact with one another<br>• The ions are 100% spherical<br>• The charge on each ion is evenly distributed around the centre so that each ion can be considered as point charges<br>**Experimental lattice energy** is the lattice energy calculated from a Born-Haber cycle which can differ from theoretical value as there is some degree of covalency due to polarization of the anion by the more electronegative cation |

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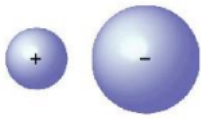
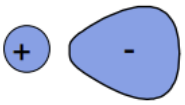
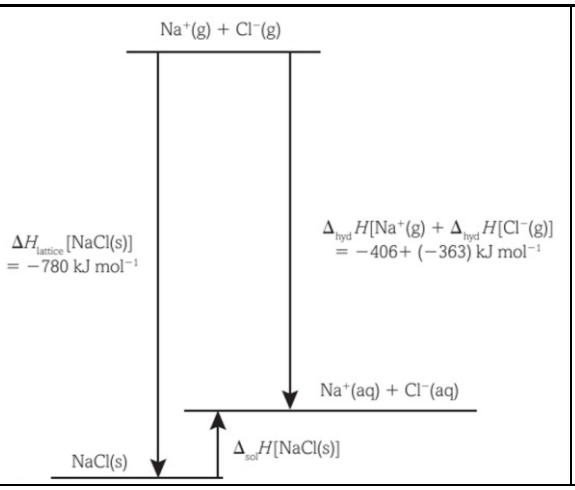
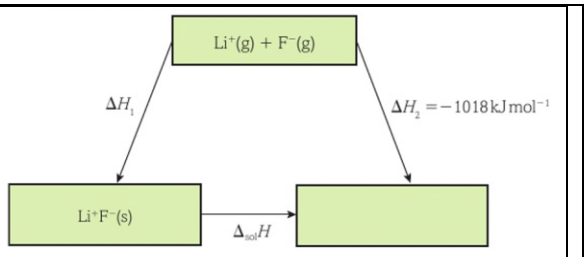
| **12.15** | understand that polarisation of anions by cations leads to some covalency in an ionic bond, based on evidence from the Born-Haber cycle |
| | Very little difference between the experimental and theoretical lattice energies indicate that the ionic model is suitable for that particular compound<br>A considerable difference between the experimental and theoretical lattice energies indicates that there is considerable covalent character in the compound due to polarization of the anion<br>Polarisation is the distortion of the electron density of an anion, resulting in a higher electron density near the cation (which results in some degree of covalency in the compound)<br>Polarisation is increased by:<br>• A high charge and small size of cation (high charge density of cation)<br>• A high charge and large size of anion<br>100% ionic  <br>When 100 % ionic the ions are spherical. The theoretical and the born Haber lattice enthalpies will be the same<br>Ionic with covalent character  <br>The charge cloud is distorted .The theoretical and the experimental Born Haber lattice enthalpies will differ |
| **12.16** | be able to define the terms 'enthalpy change of solution, $\Delta_{sol}H$' and 'enthalpy change of hydration, $\Delta_{hyd}H$ of an ion' |
| | **<u>Enthalpy change of solution</u>** is *the enthalpy change when one mole of an ionic solid dissolves in water to form an infinitely dilute solution*<br>Common examples:<br>$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$<br>**<u>Enthalpy change of hydration</u>** is *the enthalpy change when one mole of an ion in its gaseous state is completely hydrated by water* (always exothermic)<br>Common examples:<br>$Na^+(g) + aq \rightarrow Na^+(aq)$<br>When an ionic solid dissolves in water, positive and negative ions are formed<br>Water is a polar molecule with a δ- oxygen (O) atom and δ + hydrogen (H) atoms which will form ion dipole attractions with the ions present in the solution<br>The oxygen atom in water will be attracted to the positive ions and the hydrogen atoms will be attracted to the negative ions |
| **12.17** | be able to use energy cycles and energy level diagrams to calculate the enthalpy change of solution of an ionic compound, using enthalpy change of hydration and lattice energy |
| | Consider a typical past paper question:<br>**2** Some energy changes are given in the table.<br>Energy change / Value / kJ mol$^{-1}$<br>Lattice energy for $CaCl_2(s)$ : −2258<br>Enthalpy change of solution of $CaCl_2(s)$ : −120<br>Enthalpy change of hydration of $Cl^-(g)$ : −364<br>Use these data to calculate the enthalpy change of hydration of $Ca^{2+}(g)$.<br>☐ **A** −1410 kJ mol$^{-1}$<br>☐ **B** −1650 kJ mol$^{-1}$<br>☐ **C** −2014 kJ mol$^{-1}$<br>☐ **D** −3106 kJ mol$^{-1}$<br>**(Total for Question 2 = 1 mark)**<br>You can solve this in either of the two ways shown below! |



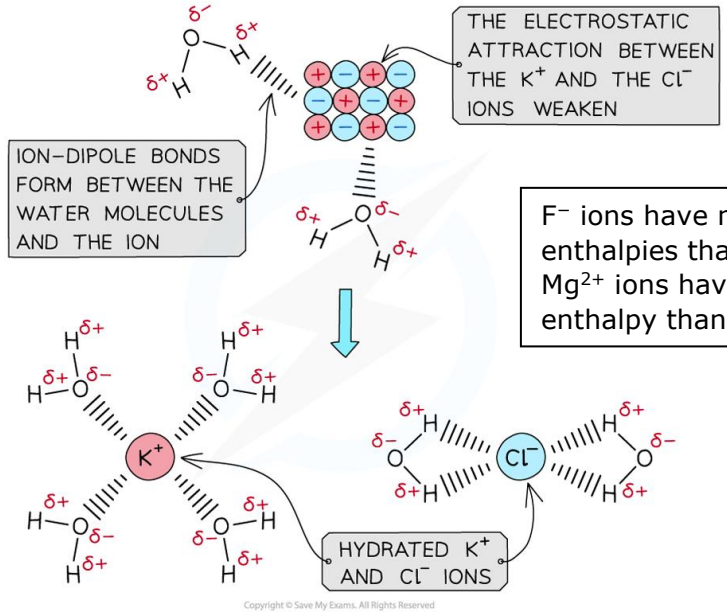




Relationship between $\Delta_{sol}H$, $\Delta_{hyd}H$ and $\Delta_{LE}H$ can be shown in both a Hess cycle or Born-Haber cycle

**12.18** understand the effect of ionic charge and ionic radius on the values of enthalpy change of hydration and the lattice energy of an ionic compound

The greater the charge density of the cation, the more the negative value of $\Delta_{hyd}H$

As we go down a group, the magnitude of $\Delta_{hyd}H$ decreases (i.e. values become less exothermic)
This is because, as we go down, the ionic radius increases while retaining the same charge, this means lower charge density which results in a decrease in the electrostatic attraction between the ions and the water molecules as the ions are less strongly attracted to the water molecules, and hence the energy released upon hydration decreases




$F^-$ ions have more negative hydration enthalpies than $Cl^-$ ions
$Mg^{2+}$ ions have more negative hydration enthalpy than $Ba^{2+}$ ions

Factors that affect Lattice Energy (of formation)

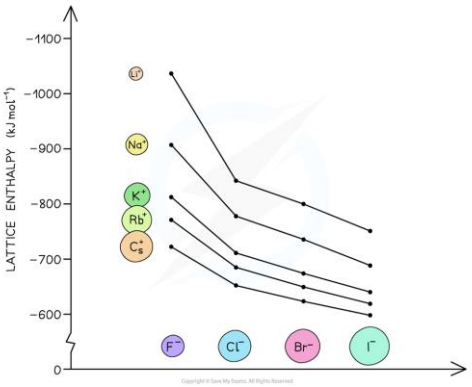
1. Magnitude of charges on the ions

(The lattice energies get more exothermic as the ionic charge of the ions increases)

This is because the greater the ionic charge, the greater the charge density
Hence, the electrostatic attraction between oppositely charged ions is stronger, resulting in more energy being required to break them
Example: LE of CaO is more exothermic than KCl as CaO consists of $Ca^{2+}$ and $O^{2-}$ while KCl consists of $K^+$ and $Cl^-$ ions

2. Sum of the ionic radii (distance between centre of cation to anion)

(The lattice energies get less exothermic as ionic radius of the ions increases)




This is because the charge on the ions is more spread out and the distance between the positive and negative ions are larger
Hence, the electrostatic attraction between oppositely charged ions is weaker, resulting in less energy being required to break them

3. Extent of covalent interactions between the ions

(The lattice energies get more exothermic as the covalent character in the compound increases)

**12.19** be able to use entropy and enthalpy changes of solution values to predict the solubility of ionic compounds and discuss trends in the solubility of ionic compounds covered in Unit 2

Factors that affect solubility of ionic compounds

1. $\Delta_{sol}H$ (standard enthalpy change of solution)
   As the $\Delta_{sol}H$ becomes more negative, solubility increases
2. $\Delta S_{total}$ (standard entropy change of the system)
   It is hard to measure $\Delta S_{total}$ so we can look at standard entropy of the ions instead
   As the entropy of hydrated ions becomes more positive, solubility increases
3. $T$ (temperature of water, in K)

Recall how the solubility of Group 2 sulfates decreases down the group while the solubility of Group 2 hydroxides increases down the group from your AS studies! Well this explains why-

<u>For group 2 hydroxides</u>,

- The entropy of hydrated ions becomes less negative down the group which means $\Delta S_{total}$ is also less negative (more positive)
- $\Delta_{sol}H$ becomes more negative down the group which means $\Delta S_{surroundings}$ becomes more positive

#Both these factors favour solubility

<u>For group 2 sulfates</u>,

- The entropy of hydrated ions become less negative down the group which means $\Delta S_{total}$ is also less negative which favours solubility
- However, the $\Delta_{sol}H$ becomes less negative down the group which means $\Delta S_{surroundings}$ becomes less positive which doesn't favour solubility

#Overall, increase in $\Delta S_{surroundings}$ > decrease in $\Delta S_{total}$

Hence, group 2 sulfates become less soluble down the group

**Further suggested practical**

Calculate the enthalpy change when a variety of ionic solids are dissolved in water